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Preparation of perfluorocarbon polymers containing phosphonic acid groups

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Abstract

Several co- and ter-fluoropolymers based on tetrafluoroethylene (TFE) and perfluorovinylethers, such as $CF_2{=}CFO(CF_2)_2P(O)(OC_2H_5)_2$, $CF_2{=}CFO(CF_2)_3P(O)(OC_2H_5)_2$, $CF_2{=}CFOCF_2CF(CF_3)O(CF_2)_2P(O)(OC_2H_5)_2$ and $CF_2{=}CFOC_3F_7$, were synthesized via redox-initiated emulsion polymerization. The products were subjected to acid hydrolysis and the corresponding fluorinated polymeric phosphonic acids were obtained. Both the polymeric phosphonates and phosphonic acids can be readily processed into films by compression molding. Perfluorinated phosphonic acid membranes with an ion-exchange capacity (IEC) within the range 2.5–3.5 milliequivalents per gram and a thermal stability of 300–350 °C were prepared. The characteristics of these acid membranes were explored, and these films show promising electrochemical properties, such as proton conductivity.

Keywords: Perfluorocarbon polymers; Phosphonic acid groups; Synthesis

1. Introduction

Co-polymers of tetrafluoroethylene (TFE) and perfluorovinylethers containing sulfonylfluorides ($-SO_2F$) or the carboxylic ester ($-C(O)OCH_3$) functionality are valuable precursors for the preparation of chemically and thermally stable cation-exchange membranes. Perfluorinated sulfonic acid membranes (Nafion) have been successfully employed as proton conductors in fuel cells based mainly on the catalytic oxidation of hydrogen [1].

The incorporation of the phosphonic acid functionality into a proton-exchange membrane (PEM) is anticipated to allow the catalytic oxidation of fuels in less acidic environments (less acidic, at least, when compared with PEMs based on polymers incorporating sulfonic acid functionalities). This lowering of acidity may allow the substitution of a relatively inexpensive metal electrocatalyst in place of the very expensive noble metal electrocatalyst found in most fuel cells to date [1].

In addition, it is expected that the phosphonic acid functionality will increase the flexibility in the PEM. The higher thermal stability and increased chemical stability of the perfluorophosphonic acid membrane, when compared with the thermal and chemical stabilities of perfluoropolymers based on sulfonic and carboxylic acid moieties, should prove advantageous when employed at temperatures greater than 100 °C.

Only a few publications have discussed the preparation and properties of perfluorophosphonic acid polymers. A free-radical autoclave telomerization of TFE with dialkyl phosphite, followed by acid hydrolysis, has provided ω-hydropolyfluoroalkylphosphonic acids ($H(CF_2CF_2)_nP(O)(OH)_2$, where $n = 1$–4) [2]. These ω-hydropolyfluoroalkylphosphonic acids have been shown to have a greater acidity than the corresponding hydrocarbon analogs. The synthesis of dimethyl(3-trifluoroethenoxyhexafluoropropyl)phosphonate ($CF_2{=}CFO(CF_2)_3P(O)(OCH_3)_2$) [3] and its bulk and solution co-polymerization with TFE in 1,1,2-trichloro-1,2,2-trifluoroethane (F113), employing 2,2′-diazobisisobutyronitrile (AIBN) as initiator [4], have also been reported. The above noted fluoropolymeric phosphonate was found to be melt processible at 170–190 °C. Acid hydrolysis of the films led to the preparation of membranes which exhibited ion-exchange capacities in the range 1.4–2.2 milliequivalents per gram (meq g^{-1}) and a conductivity at 25 °C in 1 N HCl that is slightly below Nafion. The incorporation of a third monomer, perfluoro(propylvinyl)ether ($CF_2{=}CFOC_3F_7$), has been reported to increase the flexibility of the films in the ester form. However, no further details on the polymerization reaction and no data concerning the thermal,

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mechanical and electrochemical properties of the acid films were provided [3,4].

In this paper, we report the synthesis of novel fluoropolymers based on the co-polymers and ter-polymers of TFE and the following fluorinated vinylethers: $CF_2{=}CFO(CF_2)_3P(O)(OC_2H_5)_2$ (**1**), $CF_2{=}CFO(CF_2)_2P(O)(OC_2H_5)_2$ (**2**), $CF_2{=}CFOCF_2CF(CF_3)O(CF_2)_2P(O)(OC_2H_5)_2$ (**3**), and $CF_2{=}CFOC_3F_7$. We also describe the preparation and properties of the phosphonic acid films derived from these polymeric precursors.

2. Results and discussion

2.1. *Fluoropolymeric esters (diethylphosphonates)*

Emulsion co- and ter-polymerizations initiated by a redox system operated at 18–20 °C were chosen as the most suitable for the synthesis of the desired perfluorophosphonate polymers. The simplest and least expensive redox system suitable for polymerization was sodium persulfate ($Na_2S_2O_8$) combined with sodium bisulfite ($NaHSO_3$). Emulsion polymerizations were chosen because the presence of the diethylphosphonate ester is much less likely to produce unwanted chain-transfer reactions in an aqueous system than in an organic solvent system. Emulsion polymerization also allowed a much lower concentration of the expensive phosphonate ester-containing monomer to be successfully employed. Emulsion polymerizations employing redox-initiating systems also allow mild conditions to be employed, i.e. low temperature and relatively low TFE pressures.

Co-polymers of TFE with the following functional monomers were synthesized: diethyl(3-trifluoroethenoxyhexafluoropropyl)phosphonate ($CF_2{=}CFO(CF_2)_3P(O)(OC_2H_5)_2$, **1**), diethyl(2-trifluoroethenoxytetrafluoroethyl)phosphonate ($CF_2{=}CFO(CF_2)_2P(O)(OC_2H_5)_2$, **2**), and diethyl(5-trifluoroethenoxy-4-trifluoromethyl-3-oxa-perfluoropentyl)phosphonate ($CF_2{=}CFOCF_2CF(CF_3)O(CF_2)_2P(O)(OC_2H_5)_2$, **3**). Occasionally, a third co-monomer, perfluoro(propylvinyl)ether ($CF_2{=}CFOC_3F_7$, PPVE), was added to the polymerization. In a typical experimental procedure, a solution of emulsifier ($C_7F_{15}C(O)ONa$), buffer ($Na_2HPO_4 \cdot 7H_2O$) and redox-initiating system ($Na_2S_2O_8$ and $NaHSO_3$) was prepared. Then the functional monomer was added under agitation and a flow of nitrogen. Next, the emulsion was charged into an evacuated 50 ml Parr Hastalloy-C pressure reactor, and TFE pressure was applied and maintained throughout the experiment. The co-polymerization was terminated on reaching a maximum and steady rate of TFE consumption. After coagulation, the polymer was washed and dried. Table 1 summarizes the results of the preparation of various co- and ter-polymers in ester form using varying conditions.

Fourier transform IR (FT-IR) proved to be a useful technique for monitoring the co- and ter-polymerizations. All the polymers noted above demonstrated a strong stretching vibration at 1025–1027 cm^{-1} due to the P–O–C linkages present in the phosphonate esters. Brace [2] demonstrated that stretching frequencies at 1025–1027 cm^{-1} represent the P–O–C linkages in fluorinated phosphonate esters. Polymers that contained PPVE as co-monomer showed medium to strong stretching vibrations at 993–994 cm^{-1}, demonstrating the incorporation of PPVE into the functional polymer. Kato et al. [4] claimed that, when PPVE was incorporated into fluorinated phosphonate polymers, a stretching vibration at 993–994 cm^{-1} due to the C–O–C linkages of PPVE was observed. Polymers resulting from TFE and functional monomer **3** showed strong stretching vibrations at 982–983 cm^{-1}, supporting the incorporation of the side chain ($CF_2CF(CF_3)OCF_2CF_2$) of monomer **3**. It has been shown that stretching vibrations due to the C–O–C linkages of fluorinated side chains, like those found in functional monomer **3** [1], occur at 982–983 cm^{-1}. All the polymers displayed typical, very strong, stretching vibrations in the 1100–1400 cm^{-1} region due to the C–F bonds.

Table 1
Preparation of functional fluoropolymers containing diethylphosphonate ester groups in a 50 ml Parr microreactor

Monomer (g)	TFE pressure (psi)	Time (min)	Polymer yield (g)
1 (1.50)	120–126	380	0.59
1 (1.50), PPVE (0.30)	120–126	420	0.47
2 (1.20)	120–125	500	0.50
2 (1.20), PPVE (0.24)	120–125	590	0.32
3 (1.60)	72–75	275	0.35

The hydrolysis of the fluoropolymeric diethylphosphonates to the corresponding phosphonic acids was found to be cumbersome. Typically, the hydrolysis reaction took 310–330 h at 90–100 °C using a 4 : 1 mixture of concentrated hydrochloric acid (HCl) and glacial acetic acid (CH_3CO_2H). Therefore an alternative method to determine which samples were of suitable composition and ion-exchange capacity (IEC) was developed. A quick, semi-quantitative evaluation of the amount of phosphonate ester groups contained in the polymer was developed using both thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses.

All TG analyses of the polymeric phosphonate esters showed an initial weight loss between 240 and 310 °C, as illustrated in Fig. 1. In addition, DSC analyses of the polymeric phosphonate esters showed an initial endotherm (H_a) at 275–285 °C, as illustrated in Fig. 2. The thermal decomposition of the diethylphosphonate esters to the corresponding phosphonic acids (as shown in Scheme 1), by the loss of ethylene, caused the initial weight loss in TG analysis as well as the endotherm in DSC. The TG weight loss and DSC endotherm were not present in the corresponding analyses of the hydrolyzed (phosphonic acid) samples. In addition, when the phosphonate esters were thermally pretreated by heating to 240–250 °C for 2 h, they did not display the initial decom-

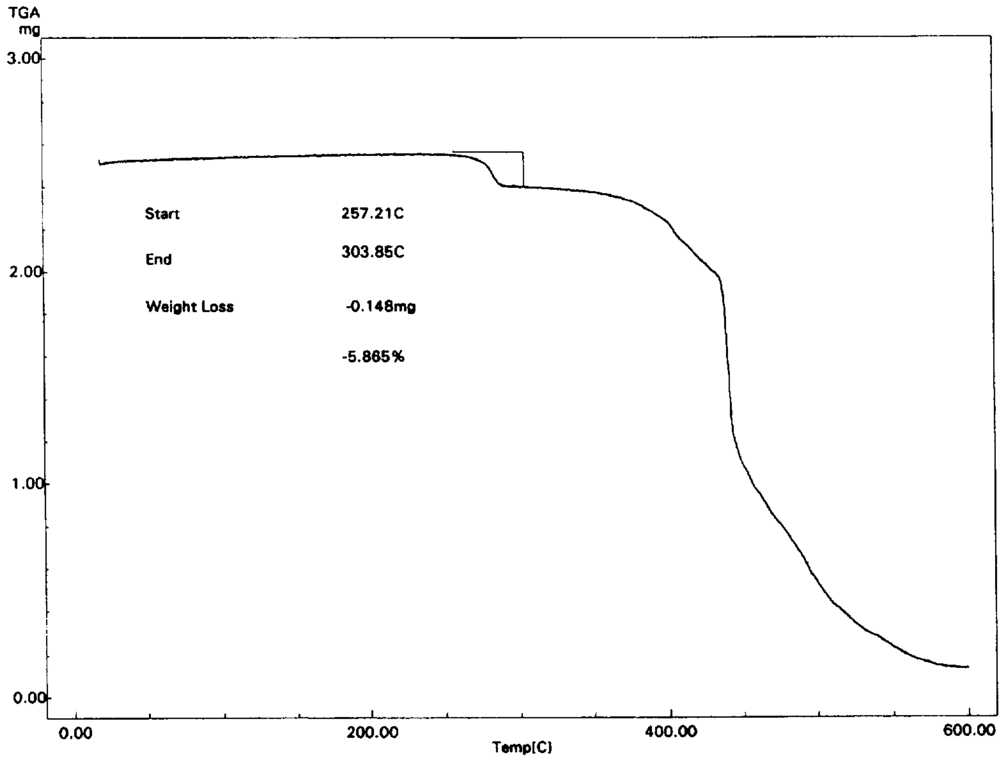


Fig. 1. Typical TG spectrum for a fluoropolymeric diethylphosphonate.

position step in TG analysis nor the initial endotherm in DSC analysis. Finally, TG analysis showed the onset of decomposition at the same temperature as DSC analysis showed the onset of the initial endotherm. The endset of the initial decomposition in TG analysis was also approximately the same as the endset of the initial endotherm in DSC analysis. It was concluded that the initial decomposition in TG analysis and the initial endotherm in DSC analysis were due to the loss of ethylene from the phosphonate esters to form the polymeric phosphonic acids.

The initial decomposition and loss of ethylene were believed to be a strong indicator of the degree of incorporation

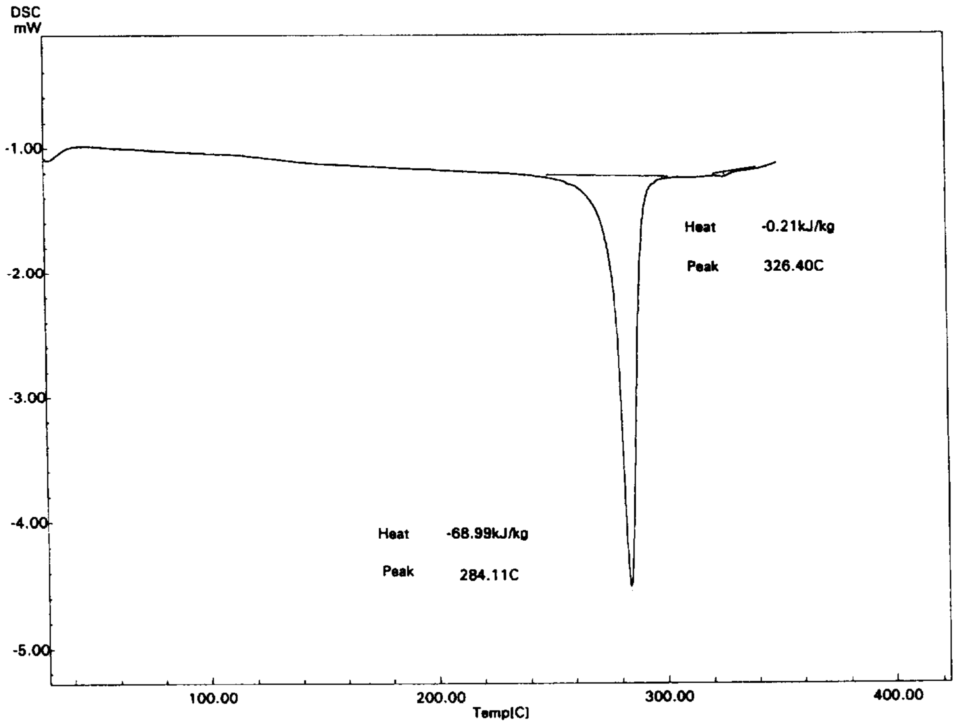
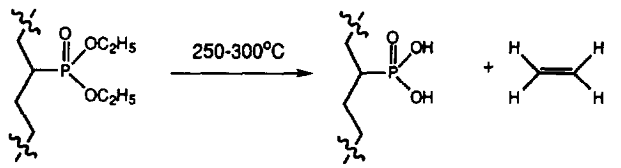


Fig. 2. DSC spectrum of a fluoropolymeric diethylphosphonate (powder) based on functional monomer **1** and TFE.



Scheme 1. Thermal decomposition of perfluoropolymeric diethylphosphonates to the corresponding perfluoropolymeric phosphonic acids.

of phosphonate ester groups into the newly formed polymeric powders. Simple stoichiometric calculations yielded a relationship between the weight loss in TG analysis (W, expressed as the percentage by weight) and the expected ion-exchange capacity ($\mathrm{IEC}_{\mathrm{exp}}$, expressed in meq g^{-1}). The constant of 28 is the molecular weight of ethylene which is lost in the reaction, and the constant of 10 is left from the conversion of units from millimoles to milliequivalents.

$$\mathrm{IEC}_{\mathrm{exp}}=\frac{10(W)}{28}$$

Several polymerizations were completed and the products were hydrolyzed to compare the calculated $\mathrm{IEC}_{\mathrm{exp}}$ value with the actual IEC, as found by back-titration of the polymeric acids. Table 2 shows three samples, together with their TG initial weight loss, actual IEC and calculated value for $\mathrm{IEC}_{\mathrm{exp}}$. Comparison shows a strong correlation, and this procedure could be used to estimate rapidly the composition of polymers before they were completely hydrolyzed. Those samples that showed a very small initial weight loss, and thus a small $\mathrm{IEC}_{\mathrm{exp}}$ value, could be discarded and the cumbersome hydrolysis need not be completed.

A second endotherm (H_b) with a peak at 324–330 °C, very close to the melting temperature of poly(tetrafluoroethylene) (PTFE), was also observed in the DSC spectra of the polymeric samples, as shown in Fig. 2. This effect was much more pronounced in co-polymers having a low IEC after hydrolysis. A second qualitative method to estimate the amount of functional monomer incorporated into the polymer involved the evaluation of the ratio H_b/H_a. Table 3 shows the correlation between the H_b/H_a ratio and IEC. The smaller the ratio, the larger the amount of functional monomer incorporated into the polymer. The endotherm H_b resulted from the excessive development of TFE block fragments in the polymeric chain, accompanied by a comparably lower content of functional groups. The higher "PTFE-like" crystallinity, combined with the reduced IEC, for some of the samples contributed to the poor quality and brittleness of the corresponding ester films of 0.12–0.18 mm thickness. Films were prepared by compression molding of the powders at 170 °C for 2–3 min. Clear, flexible films of perfluorinated polymeric esters were obtained only when nearly amorphous co-polymeric and ter-polymeric powders were used in compression molding. The best overall films of the polymers of the functional monomers **1**, **2**, and **3** were produced with powders with IECs in the range 2.0–2.2 meq g^{-1} and small H_b/H_a ratios, indicating very little PTFE block fragmentation.

Table 2
Correlation between IEC and TG/DSC data for co-polymers of TFE and functional monomer **1**

Entry	TG initial weight loss (%)	DSC, H_a (kJ kg^{-1})	IEC (meq g^{-1})	$\mathrm{IEC}_{\mathrm{exp}}$ (meq g^{-1})
1	4.0	36.4	1.7	1.4
2	4.4	40.8	1.9	1.6
3	5.7	50.9	2.2	2.0

Table 3
PTFE block fragmentation as it relates to IEC after hydrolysis for specific co-polymers of TFE and functional monomer **1**

Entry	IEC (meq g^{-1})	H_b/H_a ratio in DSC
1	1.5	0.24
2	2.2	0.025
3	2.6	0.000

2.2. *Fluoropolymeric phosphonic acids*

Early attempts to hydrolyze the ester films to the corresponding acid films resulted in the preparation of phosphonic acid films of poor quality. Poor quality is defined as brittle, unclear, and brown in color. Therefore a new approach to the problem was developed. The ester powders were first hydrolyzed, and the powdery, air-dried polymeric phosphonic acids were then hot pressed at 215–240 °C. This temperature range was employed, because it is slightly above the anticipated glass transition observed in DSC analysis. Complete hydrolysis was recognized by the disappearance of the absorption band at 1026–1028 cm^{-1} in the FT-IR spectrum (due to the P–O–C linkage of the phosphonate esters). Almost clear and relatively flexible acid films of 0.10–0.14 mm thickness were obtained, provided that a sufficient IEC and low H_b/H_a ratio were observed. In addition, no significant change in IEC occurred after film formation at elevated temperature, thus indicating a high thermal stability of the fluoropolymeric phosphonic acids. Table 4 shows five samples together with their IECs before hot pressing of the acid powders and after hot pressing to form the acid films. There were no significant changes after hot pressing the acid powders to the acid films.

The fluoropolymeric phosphonic acids, both the powders and the films, showed very different TG and DSC spectra

Table 4
Comparison of IEC before and after compression molding of powders to films at 215–240 °C

Monomers utilized	IEC of acid powder (meq g^{-1})	IEC of acid film (meq g^{-1})
1, TFE	2.6	2.8
1, TFE, PPVE	2.4	2.5
2, TFE	2.8	2.7
2, TFE, PPVE	3.0	2.8
3, TFE	3.2	3.0

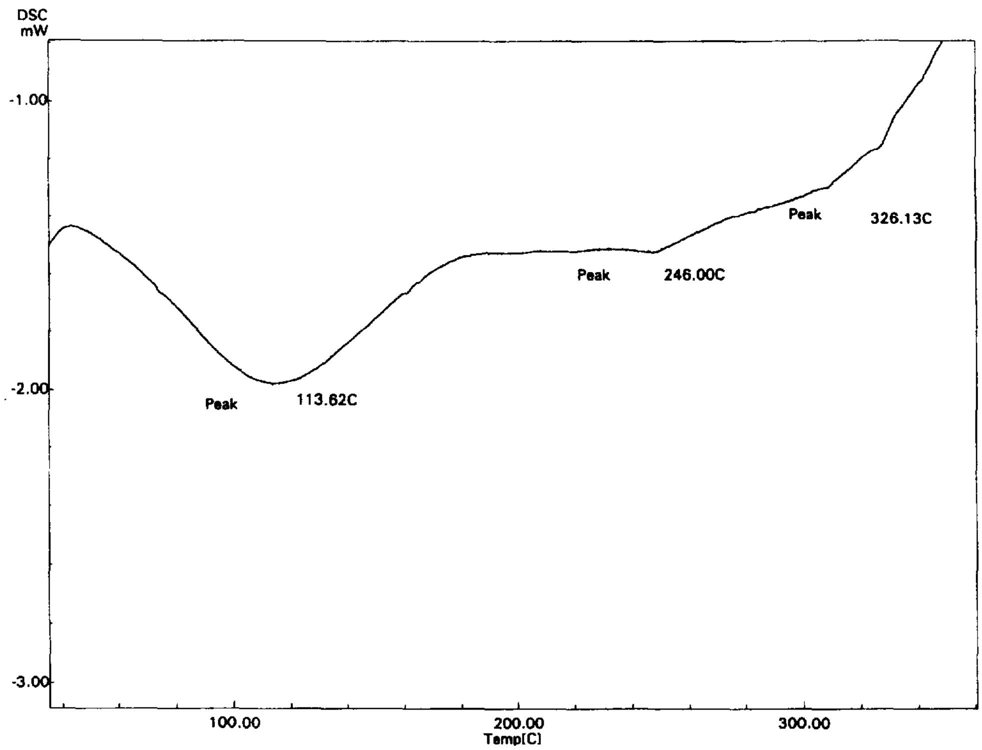
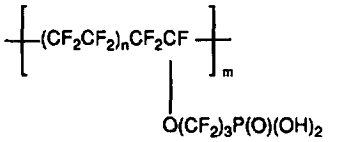


Fig. 3. DSC spectrum of a fluoropolymeric phosphonic acid (film) based on functional monomer 1 and TFE, prepared by hot pressing the acid powder at 230 °C.

Table 5
Comparison of the basic thermal properties of the fluoropolymeric diethylphosphonates and phosphonic acids

Fluoropolymeric phosphonates	Fluoropolymeric phosphonic acids
TG analysis. Initial weight loss of 5%–7% between 250 and 310 °C. Onset of rapid continuous decomposition above 300–310 °C DSC. Sharp endotherm (H_a) between 260 and 300 °C. Small endotherm (H_b) between 320 and 330 °C	TG analysis. Small weight loss of 2.0%–2.5% between 20 and 330 °C due to the loss of water. Onset of very rapid decomposition above 320 °C DSC. Broad initial endotherm at 40–180 °C due to absorbed water. No endotherm (H_a) is observed; however, if second endotherm (H_b) at 320–330 °C is present in the ester form it is preserved. There are some transitions between 200 and 250 °C for co- and ter-polymers based on monomer 1 and 2 due to the clustering of functional groups



$$\left[(CF_2CF_2)_nCF_2\underset{O(CF_2)_3P(O)(OH)_2}{\underset{|}{C}F} \right]_m$$

Fig. 4. Proposed structure of fluoropolymeric acid based on functional monomer 1 and TFE.

from their phosphonate ester precursors. Fig. 3 shows a typical DSC spectrum of a polymeric acid film. Table 5 gives a tabular comparison of the characteristics of the fluoropolymeric esters vs. the corresponding fluoropolymeric acids.

Based on the evidence obtained thus far, we propose that the structure of the fluoropolymeric phosphonic acid of functional monomer 1 is similar to that represented in Fig. 4, where the subscript n can be described by the relation: $n=(A-M_1)/M_0$. A denotes the amount of co-polymer which represents 1 mol of phosphonic acid groups or, mathematically, $A=1000/[(0.5)\mathrm{IEC}]$. M_1 is the molecular weight of the functional monomer in the acid form. For functional monomer 1, this is 328. M_0 is the molecular weight of TFE (100 mmu). For example, if the IEC of a polymeric phosphonic acid film based on functional monomer 1 and TFE was found to be 2.8 meq g^{-1}, the value of n would be 3.9. This suggests a relatively high content of the difunctional phosphonic acid groups. Each phosphonic acid group is then separated by 3–5 TFE units.

While n can be determined on the basis of IEC, the subscript m, which is an indication of the total polymer weight, cannot be determined. The fluoropolymeric esters and acids were found to be insoluble in common organic solvents even at elevated temperatures. This insolubility not only prevented the determination of the molecular weight by flow rate testing, but also prevented the casting of thin films using solutions of the polymeric powder in low-boiling solvents. For this reason, all films were made by compression molding.

The fluoropolymeric phosphonic acid films with a thickness of 0.100–0.130 mm, prepared by hot pressing the corresponding acid powders at 215–240 °C, were subjected to a

Table 6
Preliminary electrochemical evaluation of fluoropolymeric phosphonic acid films

Monomers employed	IEC of acid film (meq g^{-1})	Water absorption (%)[a]	Proton conductivity (S cm^{-1})[b]
1, TFE	2.8	22	0.076
1, TFE, PPVE	2.5	17	0.051
2, TFE	2.7	21	0.069
2, TFE, PPVE	2.8	11	0.035
3, TFE	3.0	54	0.006
Nafion	–	30	0.07–0.08

[a] Measured after boiling in deionized water for 4 h. [b] Measured at 80 °C under saturated water vapor.

preliminary electrochemical evaluation. Some properties of the acid films, associated with their possible application, are shown in Table 6. While no clear correlation could be established between the IEC and water absorption, or IEC and proton conductivity, there does appear to be a relationship between the water absorption and proton conductivity for co- and ter-polymers involving the straight-chain functional monomers **1** and **2**. Table 6 shows that a polymer of TFE and functional monomer **1** or **2** has a fairly high absorption of water, and a proton conductivity similar to commercial Nafion. When PPVE is included in a polymer involving functional monomer **1** or **2**, both the water absorption and proton conductivity decrease proportionally. We conclude that the inclusion of PPVE does not offer any advantage in either water absorption or proton conductivity at 80 °C.

The perfluoropolymeric phosphonic acid films based on TFE and functional monomer **3** show high values of water absorption. However, these films show a very low proton conductivity at 80 °C (Table 6); indeed, it is lower by an order of magnitude than the values observed for the polymeric acids of functional monomers **1** and **2** and *Nafion*. Close scrutiny of the DSC spectra of these polymeric films gives some indication as to why the conductivity is lowered. The DSC spectra of these polymeric acid films show no shift towards higher temperatures for the first endotherm after hot pressing of the acid powders. The DSC spectra of perfluoropolymeric phosphonic acids based on functional monomers **1** and **2** generally show a shift towards higher temperatures for the initial endothermic peak. This initial endotherm is believed to be caused by a glass transition of the clusters of functional groups within the polymeric film [1]. These clusters of functional groups usually act as a separate phase within the film, and are responsible for the proton conductivity. A shift towards higher temperatures after hot pressing usually indicates high cluster formation in the film. A lack of a shift towards higher temperatures for this glass transition in films based on functional monomer **3** indicates that there is poor cluster formation in the polymeric film during hot pressing. This, in turn, produces the lower proton conductivity.

3. Experimental details

TFE and $C_7F_{15}C(O)ONa$ were obtained from PCR, Inc., and were used without further purification. The functional monomers **1**, **2** and **3** were synthesized by the methods described in Ref. [5]. PPVE was obtained from E.I. duPont deNemours, and was used without further purification. $Na_2HPO_4 \cdot 7H_2O$, $Na_2S_2O_8$ and $NaHSO_3$ were obtained from Aldrich Chemical Co., and were used without further purification. FT-IR spectra were recorded on a Mattson Cygnus 100 spectrophotometer as KBr pellets. TG analyses were conducted on a Shimadzu thermogravimetric analyzer over a temperature range of 20–500 °C at a rate of increase of 10 °C min^{-1} under a flow of nitrogen (25 ml min^{-1}). DSC was performed on a Shimadzu calorimeter over a temperature range of 20–350 °C at a rate of increase of 10 °C min^{-1} under a flow of nitrogen (25 ml min^{-1}). The swelling and solubility tests were conducted by placing 0.02–0.05 g of finely ground powder samples in small beakers containing 1–2 ml of the organic solvent of choice (*N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), diethyleneglycol monomethyl ether (Diglyme), methanol, isopropanol, etc). The samples were stirred at room temperature for 24 h, and then the temperature was raised slowly to 100–150 °C, depending on the boiling point of the solvent. The solubility and/or swelling was determined by visual inspection. The water absorption and conductivity measurements were conducted at Case Western Reserve University employing the methods described by Savinell et al. [6]. The IECs of the acid powders and films were determined by immersing accurately weighed samples into 0.1 N NaOH and stirring for 24 h at room temperature, followed by back-titration with 0.1 N HCl.

3.1. Preparation of fluoropolymeric diethylphosphonates

In a general procedure, the polymerization apparatus was evacuated overnight, followed by three consecutive flushes with nitrogen, and a final evacuation. Then 0.4 g (0.9 mmol) of $C_7F_{15}C(O)ONa$, 0.3 g (1.1 mmol) of $Na_2HPO_4 \cdot 7H_2O$, 0.2 g (0.8 mmol) of $Na_2S_2O_8$ and 0.1 g (1.0 mmol) of $NaHSO_3$ were completely dissolved in 45 ml of deionized water in a small beaker. The functional monomer (**1**, **2** or **3**; 1.2–1.6 g) was added, and provisions were made to obtain a stable, oxygen-free emulsion by stirring while flushing with nitrogen. If necessary, the same procedure was repeated after introduction of a second monomer, PPVE (0.25–0.35 g, 0.9–1.1 mmol). The emulsion was immediately poured into a glass vessel which was connected to the reactor and kept under a constant flow of nitrogen. The liquid was then charged into the 50 ml Parr Hastalloy-C microreactor. The stirring speed was adjusted to 250–300 rev min^{-1}, and TFE was carefully introduced from a 500 ml stainless-steel bomb until the desired pressure (72–126 psi) was established. The desired TFE pressure was dependent on the monomer being used. Next, the stirring speed was increased to 550 rev min^{-1} and the temperature was maintained at 18–20 °C by external cooling in an ice bath. The TFE pressure was kept within a range of 4–6 psi throughout the experiment. The course of the reaction was followed by measuring the rate of TFE consumption. Consumption was high at the onset of the experiment, then dropped significantly, followed by a steady increase, until it gradually reached a nearly constant value. At this stage, the reaction was terminated and the unreacted TFE was returned to the 500 ml stainless-steel bomb. The polymeric latex was transferred to a beaker, and was coagulated using 5–10 ml of concentrated HCl, depending on the amount of product expected. The resulting mixture was then thoroughly washed with deionized water, while being slowly filtered under suction from a water aspirator. The powder was rinsed and filtered until the filtrate was neutral to pH paper and foaming due to the emulsifier was eliminated. Finally, the polymer was rinsed with methanol, filtered and dried in vacuo at 110–120 °C overnight.

3.2. *Preparation of the films by hot pressing*

In a typical preparation, 0.20–0.70 g of a dry polymeric sample was placed into a rectangular opening (6.45–10.32 cm^2), cut in the middle of a 10.1 cm × 10.1 cm aluminum foil shim of 0.5–1.3 mm thickness, inserted between two thinner (0.5 mm) sheets of aluminum foil. The foil assembly was placed between two stainless-steel plates (10.1 cm × 10.1 cm), 1.5–2.0 mm thick. The entire assembly was then placed between the hot plates of a Carver hydraulic press, that had been preheated to the desired temperature. The temperatures employed were 170 °C for ester powders and 215–240 °C for acid powders. The sample was then equilibrated to the pressing temperature for 2–3 min without application of any pressing force. The desired amount of pressure was then applied to the assembly. The amount of force was determined by the sample being processed. Ester polymeric powders were melt processed at 400–600 psi and acid polymeric powders were melt processed at 900–1100 psi. These pressures corresponded to 1.1–2.5 metric tons on the ram of the press. The pressure was applied for 2–3 min. The plates of the press were then quickly cooled to room temperature via water cooling, while the sample was kept under pressure. The pressure was released, and the stainless-steel plates were pulled apart. The aluminum foil sheets were then cut to the approximate dimensions of the film. The aluminum foil adhered to the polymeric film, and was removed by dissolving in concentrated HCl for 25–30 min. The film was completely rinsed of concentrated HCl and aluminum salts by consecutive boilings and rinsings in deionized water. Finally, the film was dried in vacuo overnight at room temperature.

3.3. *Preparation of fluoropolymeric phosphonic acids by hydrolysis of the ester precursors*

3.3.1. *Polymeric powders*

In a typical powder hydrolysis, 0.10–0.30 g of dry sample was placed into a 50 ml round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and an oil bath. This was followed by the addition of 30–40 ml of a 4 : 1 mixture of concentrated HCl and glacial acetic acid (by volume), and the solution was heated at reflux employing vigorous stirring for 300–330 h. The hydrolyzed sample was washed with deionized water and filtered slowly under suction from a water aspirator until the filtrate was neutral to pH paper. The product was then rinsed with methanol and dried according to its intended use: overnight at room temperature for the preparation of films, or in vacuo at 100–110 °C for IEC determinations.

3.3.2. *Polymeric films*

In a typical film hydrolysis, two to four films (2 cm × 3 cm, 0.12–0.16 mm thick) were immersed in 150–200 ml of a 4 : 1 mixture of concentrated HCl and glacial acetic acid. The samples were held flat to the bottom of a specially designed glass reactor using glass rings. The mixture was stirred moving the films. The mixture was then heated at 90 °C for 300–330 h. The hydrolyzed sample was washed with deionized water and filtered slowly under suction from a water aspirator until the filtrate was neutral to pH paper. The product was finally dried in vacuo at room temperature overnight.

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